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Anders Broo and Michael C. Zerner

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

University of Florida  
Department of Chemistry  
Gainesville, FL 32611 USA

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# On the Emission Spectrum of p-N,N-dimethylaminobenzonitrile.

Anders Broo and Michael C. Zerner

*Quantum Theory Project*

*University of Florida*

*Gainesville, Florida 32611-8435*

## ABSTRACT

absorption and emission spectra of p-N,N-dimethylaminobenzonitrile (DMABN) and 6-cyanobenzquinuclidine (CBQ) in different solvents. The dual fluorescence of DMABN is discussed in terms of internal twisting of the excited state as well as in terms of N-inversion of the dimethylamino group. The results indicate that the N-inversion mechanism can't explain the dual fluorescence without a twisting of the dimethylamino group.

## 1. Introduction.

In 1992 Karelson and Zerner presented a self-consistent reaction field (SCRF) method for calculating absorption spectra [1a]. The solvent relaxation was treated in a perturbative way. Recently Broo and Zerner presented a SCRF method that accounts for full electronic relaxation of the solvent [1b]. The fully relaxed SCRF has previously been used by Broo and Larsson for absorption spectra [2a] and later extended to account for an elliptical cavity shape [2b] and to treat emission spectra [2c]. However, a derivation of the method were not given in those works.

Among the most studied fluorescence spectrum is probably the dual fluorescence found in para-dimethylaminobenzonitrile (DMABN), figure 1. Lipert et al. [3] originally observed the phenomenon and assigned the two bands to two different electronic states, one strongly polar ( $^1L_a$ ) and a second which is less polar ( $^1L_b$ ). Later Khalil et al. [4] ascribed the phenomenon to excimer formation in the excited state. A third explanation was put forward by Rotkiewicz et al. [5], in which they assumed that the emission occurred from two different conformers of the excited state, one planar conformer ( $B^*$ ) and one in which the dimethylamino group had rotated 90 degrees and was perpendicular to the benzonitrile plane ( $A^*$ ). They described the excited state as a twisted intramolecular charge transfer (TICT) state. The reaction scheme for the TICT model for DMABN is depicted in figure 1. The latter explanation is nowadays commonly accepted [6] but some new alternative explanations of the dual fluorescence of DMABN are still being put forward [7]. In this alternative interpretation of the dual fluorescence of DMABN the N-inversion vibration mode of the dimethylamino group is assumed to decouple the cyano lone-pair from the  $\pi$ -electrons of the phenyl ring. However, neither the results from this work nor results from a CASSCF/CASPT2 by Roos and co workers [8] supports this alternative explanation without a rotation of the dimethylamino group.

An experimental "proof" for the TICT mechanism was obtained when Rotkiewicz et al. [9] synthesized and characterized the photochemistry of 6-cyanobenzquinuclidine (CBQ), figure 2. CBQ is an analog compound to DMABN where the amino group is fixed in a nearly orthogonal conformation with respect to the benzonitrile plane. The fluorescence spectrum of CBQ has just one broad band at about the same energy as the low energy band ( $A^*$ ) of the fluorescence spectrum of DMABN. In this work we calculate the geometry and the absorption and fluorescence spectra of DMABN and CBQ in different solvents.

## 2. Computational Details.

All calculations have been performed with the ZINDO program package [10]. The geometry optimization of DMABN and CBQ have been done with the INDO/1 Hamiltonian. The geometry of DMABN was optimized with the  $C_{2v}$  symmetry restriction. When using the  $C_{2v}$  symmetry restriction we can obtain both a planar excited state geometry and a twisted excited state geometry. However, we force the dimethylamino group to be planar with this choice of symmetry. A second optimization of the ground state of DMABN without any symmetry restrictions was performed to estimate the size of the error we introduce by restricting the geometry to  $C_{2v}$  symmetry. The geometry we obtained from the latter optimization agrees very well with the  $C_{2v}$  symmetry geometry and the dimethylamino group was still planar. The INDO/1 geometry is compared with experimental geometries and other calculated geometries in table 1. The geometry of the ground state and the first excited state of CBQ was also obtained

from an INDO/1 optimization. No symmetry constraints were used when the CBQ geometry was optimized. The excited state geometries of both DMABN and CBQ were obtained using a singlet restricted open-shell Hartree-Fock (ROHF) approach.

All spectra were calculated with the INDO/S Hamiltonian. All possible single excitations from all occupied orbitals of  $\pi$  type and lone-pair type to all virtual  $\pi^*$  type and lone-pair\* type orbitals were included in the spectra calculations of DMABN. With this selection of the CI space a total of 257 configurations were included in the CI calculation. The CI space for CBQ was obtained in a similar way and a total of 232 configurations were included in the spectral calculations of CBQ.

In this work we have used a spherical solvent cavity. The cavity radius is obtained from the mass density formula [1a] and is 3.87 Å for DMABN and 4.18 Å for CBQ. With this selection of cavity the molecules are completely enclosed in the solvent free sphere.

### 3. Results and Discussion.

In table 2 calculated absorption spectra of DMABN, in different solvents are compared with experimental absorption spectra. The character of the two first excited state is not change by the solvent. The  $1^1A \rightarrow 2^1A$  transition is the most intense absorption and is due to a  $\pi \rightarrow \pi^*$  transition (HOMO  $\rightarrow$  LUMO, 91 %). We have choosed to use the  $C_2$  symmetry labels since we are also consider a rotation around the symmetry axis that lower the symmetry to  $C_2$  during the rotation. The transition moment is along the molecular axis, from the benzonitrile group to the dimethylamino group. The character of the second transition ( $1^1A$  to  $1^1B$ ) is also a  $\pi \rightarrow \pi^*$  transition (HOMO-1  $\rightarrow$  LUMO, 22% and HOMO  $\rightarrow$  LUMO+1, 76%). The transition moment is perpendicular to the first transition moment and is in the benzonitrile plane.

All absorption energies are calculated slightly too low compared to the experimental energies. The calculated solvent shift between cyclohexane and pyridine is underestimated, likely because the calculated dipole from each excited  $1^1A$  state is underestimated. Using the experimental dipole of 17.0 Debye and first order perturbation theory yields a shift of 1200  $\text{cm}^{-1}$ , to be compared with the observed shift of 1600  $\text{cm}^{-1}$  and our calculated value of 800  $\text{cm}^{-1}$ .

One test calculation with the INDO/1 geometry and with the experimental wagging angle of the dimethylamino group (12 degrees) was preformed. The wagging vibrational mode of the dimethylamino group corresponds to a change in hybridization of the nitrogen atom from  $sp^2$  to  $sp^3$ . The predicted energies was shifted up to higher energies by 1600  $\text{cm}^{-1}$  for the  $1^1B$  state and 900  $\text{cm}^{-1}$  for the  $1^1A$  state. Furthermore, a small decrease in dipole moment was observed. These observations argue against the N-inversion mechanism for the dual fluorescence of DMABN proposed by Zachariasse et al. [7,14]. However, to be consistent we kept the INDO/1 geometry in all further calculations.

The predicted absorption spectra of CBQ in methanol are compared with experimental spectra in table 3. The positions of the absorption maximum of CBQ are almost solvent independent; thus, we report only the calculated absorption spectrum in one solvent. The small solvent shift of the major peaks is due to the small change in the charge distribution upon excitation. In the region of 31000-37000  $\text{cm}^{-1}$  three weak peaks appears in the calculation but the strong peak calculated at 37000  $\text{cm}^{-1}$  and observed at 35000  $\text{cm}^{-1}$  might be expected to mask these transitions in the experimental spectrum. The first weak transition corresponds to a charge transfer from the

amino group to the benzonitrile group with transition moment polarized along the molecular axis ( $n \rightarrow \pi^*$ ). The two other weak peaks are of  $\pi \rightarrow \pi^*$  type. In polar solvents such as acetonitrile a shoulder at about  $32000 \text{ cm}^{-1}$  is experimentally observed [9]. The first two major peaks have  $\pi \rightarrow \pi^*$  character and the transitions are localized to the benzonitrile group.

The accuracy of the above results give us confidence to apply the fully relaxed SCRF theory to the emission problem [1b,2]. The potential energy surfaces, as a function of time and twist angle of the dimethylamino group, for the two first excited states of DMABN are depicted in figure 3. The surfaces in figure 3 corresponds to these calculated for an acetonitrile solution. At time zero the potential energy surfaces for the absorption are displayed and corresponds to complete electronic relaxation of the solvent, but no nuclear relaxation of either solute or solvent. At arbitrary time "ten" the relaxed state generation of the chromophore is used, and the solvent is allowed to dielectrically relax. The time axis displays the relaxation of the excited states due to solvent and solute rearrangement in arbitrary units. The potential energy surfaces for other solvents were also calculate, but are not shown here. In gas phase we predict a small barrier for the twisting of the  $^1A$  state of  $2.9 \text{ kcal/mol}$ , while in cyclohexane the barrier is only  $0.6 \text{ kcal/mol}$  and in the two polar solvents the barrier vanishes. The INDO method is not expected to give high accuracy in the calculation of rotational barrier so these numbers can not be used with great confidence. However, the trend is in good agreement with the observed facts that in non-polar solvents the fluorescence spectrum has only one peak ( $B^*$ ), while in polar solvents two peaks appears.

The predicted fluorescence spectra of DMABN in different solvents are summarized in table 4. The initial state for the fluorescence is the lowest singlet excited state,  $S_1$ . Furthermore, the initial state is long-lived and the molecule and the solvent have time to fully relax before the emission takes place. Because of this relaxation the fluorescence spectrum is red-shifted compared to the absorption spectrum. This shift is called the Stokes shift. The calculated Stokes shift for the high energy band is ranges between  $2400 \text{ cm}^{-1}$  in cyclohexane and  $3500 \text{ cm}^{-1}$  in acetonitrile to be compared to an observed Stokes shift of about  $6500 \text{ cm}^{-1}$  for all solvents. The Stokes shift for the low energy band is calculated to be between  $7200 \text{ cm}^{-1}$  and  $12100 \text{ cm}^{-1}$  compared to the observed Stokes shift  $9500 \text{ cm}^{-1}$  to  $12900 \text{ cm}^{-1}$ . The solvent shift of the two fluorescence peaks when going from non-polar solvents to polar solvents is calculated to be  $1900 \text{ cm}^{-1}$  and  $6400 \text{ cm}^{-1}$ , respectively, to be compared with experimental values of  $1600 \text{ cm}^{-1}$  and  $5000 \text{ cm}^{-1}$ .

The experimental fluorescence spectrum of DMABN in non-polar solvents has one peak but the band shape is asymmetric with a broad tail extending toward lower energies. Schuddeboom et al. resolved the tail of the emission band in cyclohexane solution by subtracting the fluorescence spectrum of 4-(methylamino) benzonitrile [14]. In medium polar solvents two separate bands can be observed and in very polar solvents the  $A^*$  band dominates and the  $B^*$  band is observed as a shoulder on the very broad  $A^*$  band. Furthermore, the lifetime of  $B^*$  state is very short, in the picosecond region, consistent with its large calculated oscillator strength. The lifetime of the  $A^*$  state is in the nanosecond region [14]. All the experimental fluorescence energies correspond to the band maximum of each peak.

In the fully twisted conformer the transition is completely forbidden and the emission most likely takes place from a vibrational excited state; i.e. "hot fluorescence". The question is then

if the calculated energies for the A\* fluorescence should be compared with the band maximum or with the low energy limit of the A\* band. From the potential energy surfaces in figure 3 we can conclude that the fully twisted conformer corresponds to a local energy minimum and every vibration along the twisting coordinate will increase the calculated fluorescence energy. Thus, we suggest that the energies we calculated for the A\* band are the low energy limit. With the above interpretation of the calculated fluorescence spectra the agreement between the calculated spectra and the experimental spectra is good and both the solvent shift and the Stokes shift are well reproduced.

The geometry of the amino group of CBQ corresponds to the twisted conformer of DMABN with a wagging angle of about 25 degrees. The experimental fluorescence spectrum of CBQ has only one band and the position of the band corresponds to the position of the A\* band in DMABN. This was taken as a proof for the TICT mechanism of the dual fluorescence but both the twisting and the wagging effect is included in the CBQ geometry. The calculated spectrum of CBQ is compared with the experimental spectrum in table 5. The calculated energies for the fluorescence should correspond to the observed band maximum tabulated in table 5. The geometry change upon excitation of CBQ is small. After solvent relaxation the S<sub>1</sub> state is still a rather polar state compared to the ground state. Thus, the fluorescence spectrum will be red-shifted compared to the absorption spectrum. The Stokes shift, in methanol, is predicted to be 12600 cm<sup>-1</sup> to be compared with the experimental value of 14600 cm<sup>-1</sup>. The calculated fluorescence spectra agrees well with the experimental spectra.

#### **4. Summary.**

We have calculated both absorption and fluorescence spectra of DMABN and CBQ in different solvents. The calculated spectra agrees well with the experimental observed spectra. The predicted solvent shift of the fluorescence spectra of DMABN is in very good agreement with the observed shift. The calculated Stokes shift is also in good agreement with the measured Stokes shift. Our calculations supports the TICT mechanism for the dual fluorescence of DMABN and the wagging vibrational activation suggested by Zachariasse et al. [7,14] seems to be less important. This conclusion was also reached by Roos et al. [8] based upon CASSCF/CASPT2 gas phase calculations.

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### Figure legends.

Figure 1. The reaction scheme for the TICT model for DMABN. The absorption takes place from the planar conformer ( $B \rightarrow B^*$ ). The planar excited state can either decay radiatively ( $k_{f,B^*}$ ) or non-radiatively ( $k_{nr,B^*}$ ) to the ground state or undergo a conformation change to the perpendicular conformer. The conformation change reaction is temperature dependent. The twisted excited state can decay radiatively ( $K_{f,A^*}$ ) or non-radiatively ( $k_{nr,A^*}$ ).

Figure 2. a) p-N,N-dimethylaminobenzonitrile (DMABN) b) 6-Cyanobenzquinuclidine (CBQ)

Figure 3. The potential energy surfaces for the two first excited states of DMABN. The potential energy surfaces are functions of the twisting angle and time. Following the time axis corresponds to relaxation due to the solvent and solute reorientation. The time axis is arbitrary.

Table 1. Comparison of calculated geometries with the crystallographic geometry from reference 11.

Bonds (Å)	HF/ STO-3G ref. 12	CASSCF ref. 8	INDO/1 g.s.	Exp. ref. 11	INDO/ ROHF exc. 0°	INDO/ ROHF exc. 90°
N1-C2	1.157	1.157	1.200	1.145	1.214	1.288
C2-C3	1.458	1.446	1.424	1.434	1.387	1.449
C3-C4	1.394	1.399	1.402	1.388	1.451	1.451
C4-C5	1.379	1.391	1.389	1.370	1.354	1.433
C5-C6	1.402	1.406	1.407	1.400	1.447	1.462
C6-N7	1.446	1.388	1.399	1.367	1.387	1.426
N7-C8	1.486	1.460	1.422	1.456	1.422	1.434
Bond angles (Degree)						
N1-C2-C3	180.0	180.0	180.0	-	180.0	180.0
C3-C4-C5	120.8	120.0	121.0	-	120.5	120.5
C4-C5-C6	121.1	121.4	120.2	-	120.8	120.9
C5-C6-N7	121.5	121.3	120.5	-	120.6	120.8
C6-N7-C8	122.4	122.2	120.1	121.6	121.0	119.1
C8-N7-C8'	115.1	115.6	119.8	116.4	118.1	121.8
Dihedral angle (Degrees)						
C5-C6- N7-C8	41.8	21.2	0.0	11.9	0.0	0.0

Table 2. Comparison of the calculated and experimental absorption spectra of DMABN in different solvents. The experimental absorptions energies are taken from reference 13 and references therein and the experimental excited state dipole moment is from reference 14.

Solvent	Calculated absorption spectrum						Experimental absorption spectrum			
	<sup>1</sup> A			<sup>1</sup> B			<sup>1</sup> A		<sup>1</sup> B	
	E (kK)	f <sub>osc</sub>	μ (D)	E (kK)	f <sub>osc</sub>	μ (D)	E (kK)	μ (D)	E (kK)	μ (D)
Cyclohexane	34.0	0.64	13.9	33.5	0.03	9.5	35.5	17.0	33.1	9.9
Pyridine	33.2	0.67	15.9	33.0	0.04	11.3	33.9	n.o.	n.o.	
Acetonitrile	33.2	0.66	16.0	33.1	0.04	11.1	33.9	n.o.	n.o.	

Table 3. Experimental and calculated absorption spectra of CBQ in methanol. Experimental spectrum is taken from reference 9.

Calculated spectrum			Experimental spectrum	
Energy (kK)	$f_{osc}$	$\mu$ (Debye)	Energy (kK)	$\epsilon_{mol}$
31.6	$8 \times 10^{-5}$	17.8		
34.3	0.04	6.9		
36.9	$2.3 \times 10^{-4}$	7.0		
37.3	0.31	9.5	35.9	3000
38.8	$2 \times 10^{-4}$	18.2		
40.7	$4 \times 10^{-5}$	7.3		
43.8	0.22	7.9	42.8	4000

Table 4. Comparison of calculated and experimental fluorescence spectra of DMABN. a) references 14, b) reference 15 and c) reference 13 and references therein.

Solvent	Planar (B*)		Twisted (A*)		Experimental (B*)	Experimental (A*)
	Energy (kK)	$f_{osc}$	Energy (kK)	$f_{osc}$	Energy (kK)	Energy (kK)
Cyclo-hexane	31.6	0.73	25.8	0.00	29.0 <sup>a</sup>	26.0 <sup>a</sup>
Benzene	31.5	0.73	25.4	0.00	28.9 <sup>a</sup>	24.0 <sup>a</sup>
Dioxane	31.5	0.73	25.4	0.00	28.3 <sup>a</sup>	22.7 <sup>a</sup>
Diethyl ether	30.8	0.74	22.8	0.00	27.8 <sup>b</sup>	23.4 <sup>b</sup>
Tetrahydro-furan	30.4	0.76	21.5	0.00	27.8 <sup>b</sup>	23.0 <sup>b</sup>
Pyridine	30.1	0.76	20.9	0.00	27.4 <sup>c</sup>	22.6 <sup>c</sup>
Acetonitrile	29.7	0.77	19.4	0.00	27.4 <sup>c</sup>	21.0 <sup>c</sup>

Table 5. Comparison between calculated and experimental fluorescence spectrum of CBQ in different solvents.

Solvent	Calculated		Experimental
	Energy (kK)	$f_{osc}$ ( $\times 10^4$ )	Energy (kK)
Isooctane	29.1	2.0	25.5
Methanol	24.7	1.0	21.3

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Dr. Robert Green, Director (1)  
Chemistry Division, Code 385  
Naval Air Weapons Center  
Weapons Division  
China Lake, CA 93555-6001

Dr. Bernard E. Douda (0)  
Crane Division  
Naval Surface Warfare Center  
Crane, Indiana 47522-5000

Dr. Elek Lindner (1)  
Naval Command, Control and  
Ocean Surveillance Center  
RDT&E Division  
San Diego, CA 92152-5000

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